

## Thoroughly anomalous chromium in Orgueil

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**Abstract**—Stepwise dissolution of bulk Orgueil reveals that all of the Cr in the whole rock is isotopically anomalous, with an anomaly pattern that is thus far unique. Most of the Cr (along with other major and minor cations) is dissolved by acetic and nitric acids; it is deficient in <sup>54</sup>Cr by ~5 ‰. Subsequent treatment with hydrochloric acid dissolves a small fraction of the Cr with positive <sup>54</sup>Cr anomalies, up to ~210 ‰. Mass balance indicates that whole rock Cr is isotopically normal within analytical uncertainties. The least extravagant interpretation of these results is that some mineral phase is enriched in a heavy-Cr nucleosynthetic component, while most of the Cr is a homogenized mixture of diverse nucleosynthetic components that would be normal except for lack of the postulated heavy Cr carrier. The carrier is likely, but not necessarily, presolar interstellar grains. Its identity is unknown and constrained only circumstantially: it must be relatively rich in Cr, it is substantially soluble in hydrochloric acid, and it is not magnetite or spinel/chromite. Scanning electron microscope (SEM) examination of Orgueil reveals candidate Cr-rich oxides, silicates, sulfides and phosphides, but none of these can be identified yet as the heavy Cr carrier. Whether presolar or not, the carrier is not chemically resistant and likely not thermally refractory, thereby differing from most other phases known to host isotopic anomalies. Its survival (or production) thus establishes constraints on a different regime of nebular history.

### INTRODUCTION

Meteoritic materials are known to harbor a variety of isotopic anomalies, that is, isotopic compositional variations that cannot plausibly be understood as arising in either chemical or nuclear processes within the solar system. Instead, they must be understood in terms of compositional differences in the distinct stellar nucleosynthetic processes ultimately responsible for most of the elements that constitute the solar system. There are several "kinds" of occurrences of anomalies, which we need not attempt to review here, but one distinction relevant to subsequent discussion is worth making. There are some discrete and isolatable meteoritic phases, which have been identified as interstellar grains (e.g., see Anders and Zinner, 1993), that have maintained their separate identities throughout whatever processing they have experienced in the interstellar medium, the solar nebula, and their meteoritic parent bodies. These presolar grains typically have isotopic compositions radically different from normal solar system values (indeed, this is the primary criterion by which they are recognized as presolar) and are thought to represent specific nucleosynthetic processes occurring in individual stars. The complementary occurrences comprise cases in which isotopic compositions are only much more modestly (but still quite measurably) different from normal values. These are taken to occur in lithologic constituents that formed within the solar system from diverse materials representing many different nucleosynthetic processes, but such that one or more nucleosynthetic components is slightly over- or underrepresented relative to the mixture which defines normal solar composition.

The focus of this paper is investigation of isotopic anomalies in the element Cr in carbonaceous chondrites, thus far a unique kind of occurrence first observed by Rotaru *et al.* (1992). Most strikingly in CI meteorites such as Orgueil, stepwise dissolution of the whole rock liberates Cr with both excesses and deficiencies in <sup>54</sup>Cr. In

Orgueil and other CI meteorites, essentially all of the Cr in the whole meteorite is anomalous. The characteristic pattern is that most of the Cr, dissolved in the least aggressive reagents, is deficient in <sup>54</sup>Cr by several ‰ (0.01%) units, and a small part, dissolved in more aggressive reagents, has stronger enrichments of <sup>54</sup>Cr, up to 101 ‰ in the observations of Rotaru *et al.* (1992). In surveying other classes of carbonaceous chondrites, Rotaru *et al.* (1992) find qualitatively similar but more subdued effects in CM meteorites and only very much smaller (if any) effects in carbonaceous chondrites of petrographic grades 3 and 4. They plausibly attribute this to isotopic homogenization by parent-body metamorphism.

Excess <sup>54</sup>Cr suggests a nucleosynthetic component produced in neutron-rich nuclear statistical equilibrium (e.g., Hartmann *et al.*, 1985; Meyer, 1994) or in matter expanding from high temperature and density (e.g., Sorlin *et al.*, 1995; Meyer *et al.*, 1996). In such cases, anomalies in coproduced elements, specifically Fe-group elements, would also be expected. No correlative anomalies in any other element have yet been found, however, including Fe-group elements (see Rotaru *et al.*, 1992). The concentration of anomalies in Cr presumably reflects mineralogical control, but the nature of the hypothesized carrier phase is largely unconstrained. As yet there are also no known correlative effects in the other isotopes of Cr. (Rotaru *et al.*, 1992, observed small variations in the relative abundance of <sup>53</sup>Cr in some samples but state that these can be attributed to excesses or deficiencies of radiogenic <sup>53</sup>Cr from decay of short-lived <sup>53</sup>Mn.)

In this study, we do not attempt to extend the survey of meteorites exhibiting the Cr anomalies but instead concentrate on a single meteorite, Orgueil, and on a more detailed investigation aimed at improving constraints on the nature of the effect. Besides Cr isotopic analyses, we have also better constrained the overall chemistry of the dissolution procedures and conducted scanning electron mi-

TABLE 1. Chemical compositions at Orgueil dissolution fractions.

Sample	Treatment*	ICP-MS analyses									ID analyses	
		Mg %	Al %	Ca %	Ti ppm	Cr ppm	Mn ppm	Fe %	Ni %	Sr ppm	Ca %	Sr ppm
<b>O-I (bulk Orgueil 202 mg)</b>												
1	2.5% HAc RT 35 min	2.51	0.005	0.059	18	25	956	0.021	0.28	4.5	0.270	2.66
2	50% HAc RT 1 d	1.59	0.030	0.055	15	329	1411	0.68	0.69	4.0	0.238	2.10
3	4N HNO <sub>3</sub> RT 5 d	7.80	0.61	0.070	307	1789	1763	1.45	0.66	3.8	0.395	2.80
4	6N HCl RT 5 d	0.17	0.012	0.002	45	78	509	0.84	0.009	0.5	0.003	0.060
5	6N HCl 36 °C 1 d	0.023	0.002	0.003	28	15	14	0.014	0.002	0.1	0.001	0.012
6	6N HCl 80 °C 1 d	0.004	0.005	0.003	124	47	63	0.072	0.013	0.2	0.003	0.035
7	Conc. HF/HCl 100 °C 1 d	0.009	0.009	0.003	14	64	11	0.006	0.001	0.2		0.128
8	Repeat step 7	0.001	0.007	0.002	1	1	1	0.002	<0.001	0.1		
9†	4N NaOH 80 °C 3 h	0.010	0.012	0.003	11	110	12	0.022	0.005	1.2		
10	HClO <sub>4</sub> 185 °C 2.5 h	0.005	0.002	0.005	1	129	42	0.005	0.001	0.2		
Sum		12.1	0.69	0.21	564	2587	4782	3.11	1.66	16.8	0.91	7.8
<b>O-II (97 mg)<sup>‡</sup></b>												
5		0.006	0.001	0.007	1	2	5	0.008	0.007	0.7		
6		0.006	0.005		1	6	1	0.023	<0.001	0.1		
Al		0.004	0.002		1	10	2	0.002	<0.001	<0.1		
M1	6N HCl RT 2 d	0.004		0.060	35	154	136	2.86	0.014	1.2		
M2	6N HCl 40 °C 1 d	<0.001		<0.001	1	4	1	0.037	<0.001	0.1		
M3	6N HCl 80 °C 1 d	0.001		0.011	2	13	2	0.047	0.001	0.1		
M4	9N HCl 80 °C 1 d	0.001		0.011	2	8	2	0.038	0.001	0.1		
<b>O-III (bulk Orgueil 116 mg)</b>												
1	2.5% HAc RT 35 min	1.52	0.005	0.54	33	11	718	0.065	0.20	4.7		
2	50% HAc RT 1 d	1.16	0.056	0.32	16	526	671	6.95	0.68	2.6		
3	4N HNO <sub>3</sub> RT 5 d	6.39	0.55	0.13	233	1283	462	5.09	0.28	1.0		
4	6N HCl RT 5 d	0.032	0.004	0.018	37	14	93	6.12	<0.001	0.1		
5	6N HCl 36 °C 1 d	0.045	0.001	0.003	117	8	17	0.21	<0.001	0.1		
6	6N HCl 80 °C 1 d	0.005	0.001	0.003	46	23	8	0.20	0.005	0.1		
7	Conc. HF/HCl 100 °C 1 d	0.007		0.005	7	122	5	0.038	<0.001	0.1		
Sum		9.2	0.62	1.01	489	1987	1974	18.7	1.17	8.7		
<b>Average CF</b>												
Bulk		9.6	0.86	0.94	430	2600	1940	18.2	1.04	7.7	0.94	7.7

\*Reagent (HAc = CH<sub>3</sub>COOH), (RT = room temperature) and duration.

†This step preceded by CS<sub>2</sub> extraction intended to remove elemental S; removal of tabulated cations in the extraction is expected to be negligible.

‡Cl bulk composition listed in Kerridge and Mathews (1988).

§Bulk sample O-II (97 mg) was leached in acetic and nitric acids, as were samples O-I and O-III; the residue was then separated into "magnetic" and "nonmagnetic" fractions by adherence to a magnetic stirring bar in NaOH slurry.

roscope (SEM)/energy dispersive x-ray (EDX) examinations in search of potential carrier phases.

## EXPERIMENTAL PROCEDURES

### Samples

We analyzed three whole-rock samples of Orgueil, hereafter designated O-I, O-II and O-III, with starting weights 202 mg, 97 mg and 116 mg, respectively. Samples O-I and O-III were treated sequentially with a series of progressively stronger reagents, as listed in Table 1. After each treatment, the sample was centrifuged, and the supernatant was decanted by pipette; the residue was then washed with water, centrifuged and similarly decanted. The washing procedure was repeated twice more, and all supernatants were combined to form the solution for that step. The solutions were aliquotted. A small fraction was taken for inductively coupled plasma mass spectrometry (ICP-MS) analysis, and the larger fraction was taken for isotopic analysis. In some cases, a third (small) aliquot was taken for isotope dilution analysis of Ca and Sr concentration (see Table 1). And also in some cases, a very small fraction of the liquid (a few microliters, <0.1%) was removed, dried and inspected by SEM for a preliminary check of major element dissolution. After step 3 (nitric acid) for O-III, the residue was dried and weighed and found to be 36% of the starting weight; no special measures were taken to remove hydration in the residue (or the starting sample), however, so that

this estimate of bulk material dissolved in the first three steps is only approximate.

Sample O-II was similarly processed through steps 1–3 (acetic and nitric acids). The fourth step, however, was stirring in 30% NaOH, leading to solution O-II-4 (the supernatant) and two residue fractions, a magnetic fraction (material which adhered to a teflon-coated magnetic stirring bar) and a nonmagnetic fraction. Examination by SEM of the magnetic fraction revealed only magnetite. The magnetic fraction was further treated with reagents to yield samples O-II-Mx. The nonmagnetic fraction was treated with HCl to produce samples O-II-5 and -6, and the undissolved residue was split (~60%/40%) into samples O-II-A and -B. Further HCl treatment of O-II-A yielded sample O-II-A1.

The chemical processing of O-I was taken essentially to complete dissolution of the whole rock, so that O-I provides the best basis for assessment of mass balance; the other samples were not processed beyond the HF/HCl stage, leaving a small fraction of the Cr unexamined. Subsequent to some of the dissolution steps in the processing of O-III, small quantities of undissolved residue were removed for SEM examination. Besides general examination of the residues, the principal characterization was a search for potential Cr hosts by automated SEM x-ray mapping (see below).

### Inductively Coupled Plasma Mass Spectrometer Analyses

The solution aliquots designated for ICP-MS analysis were dried and brought back into solution in concentrated double-distilled HNO<sub>3</sub> (ultrapure

acids and 18 megohm water were routinely used in all such procedures). Then, this procedure was repeated in order to remove the matrix used in the dissolution procedure. After the second concentrated HNO<sub>3</sub> treatment and subsequent evaporation, the sample was taken up in 5 mL 2% HNO<sub>3</sub>.

Analyses by ICP-MS were conducted in the Notre Dame Fisons PQ II STE inductively coupled plasma mass spectrometer using a Meinhardt nebulizer. Gas flows were adjusted to give a relatively flat response across the mass range. Samples were analyzed in batches, as they became available. Two internal standards were used for each batch, Sm and Y at 10 ppb, or In and Y at 20 ppb. No internal standard could be found closer to the light end of the mass range (*i.e.*, there were no free masses that could be analyzed easily by ICP-MS). However, analysis of the standards as unknowns at the end of each run demonstrated that fractionation of the response curve did not occur over the time of analysis. Internal standards were prepared from SPEX single-element ICP-MS standards.

In the first batch (O-I), 0.2 mL of each stock solution was diluted up to 10 mL with 2% HNO<sub>3</sub>; this was to insure that the detector did not become saturated at major peaks (e.g., Mg, Fe). In the subsequent batches, 1 mL of the stock solution was diluted to 10 mL. The higher concentration of stock solution was used in an unsuccessful attempt to examine trace element concentrations at the higher end of the mass range. This resulted in a higher signal from the major elements, requiring each sample to be analyzed in "dual mode" (pulse counting and analog) with a detector cross calibration conducted using a 100 ppb tuning solution (containing Be, Mg, Co, In, Ce, Bi, Pb and U). Internal standards were at 20 ppb in the later batches because of the higher concentration of sample.

External standards were prepared using SPEX ICP-MS standard solutions spanning three orders of magnitude in concentration (1 ppb to 1 ppm). These external standards were prepared in 2% HNO<sub>3</sub>, the same matrix as the unknown samples. All samples, blanks and standards were analyzed four times (60 s each analysis). Reported data are for the mean of these analyses, except that if one analysis deviated from the others by >10%, it was rejected (if two or more deviated by >10%, the sample was reanalyzed). Instrument stability was checked before and after analysis with a 10 ppb tuning solution (of the type used for detector cross calibration) analyzed ten times (60 s each analysis); signal variance was at or below 2% across the mass range, demonstrating instrument stability throughout the time of analysis.

For O-I, the element concentration totals are rather high for Mn, Ni and Sr and low for Ca and Fe (but quite reasonable for Cr). We presume this to be a calibration problem, and the relative proportions appearing in each fraction are correct. The totals for O-III are reasonable.

### Thermal Ionization Isotopic Analyses

Sample solutions were dried and, if the dissolution reagent was not HCl, converted to chlorides by repeated addition of purified HCl and drying (the acetic acid samples were first similarly converted to nitrate form). Residues were dissolved in 0.67 N HCl and loaded on a cation exchange column (6 mm diameter, 2 cm high, AG50-12X 200-400 mesh resin). Chromium was eluted first in 5 mL 0.67 N HCl. For mass spectrometric analysis, Cr in 1 N HCl was loaded on Re filaments with silica gel and saturated boric acid. In one case (O-II-B), a small solid sample was directly loaded on the filament without prior dissolution (*cf.*, Simon *et al.*, 1994).

Thermal ionization isotopic analyses of Cr were performed on either of two instruments at Washington University, a VG 354 and a VG Sector 54. Samples containing a sufficient quantity of Cr were analysed in static Faraday multiple-collector mode (<sup>52</sup>Cr beam 2 × 10<sup>-11</sup> A) on the Sector 54, in some cases with vendor-supplied software and in others with in-house software; results for the two software systems were comparable. Some samples contained too little Cr to support so high an ion beam; these were analyzed at lower beam intensity (4 or 6) × 10<sup>-14</sup> A, *i.e.*, 250 or 400 keps) using a single-collector procedure with a Daly detector operated in pulse-counting mode. Daly analyses were performed on both instruments, with in-house software. Procedures for Cr analysis with the VG 354 have been described previously by Simon *et al.* (1994); this is the first report of data acquired with the Sector 54. For all analyses, we adopted the conventional choice of <sup>50</sup>Cr/<sup>52</sup>Cr = 0.051859 (Shields *et al.*, 1966) as the normalizing ratio for correction of instrumental isotopic discrimination, with mass dependence assumed to follow the "exponential" law described by Russell *et al.* (1978). All data for <sup>53</sup>Cr and <sup>54</sup>Cr (Tables 2 and 3) are reported as  $\epsilon$  values (*i.e.*, parts in 10<sup>4</sup> deviation from normal composition). Calibration analyses of terrestrial reagent Cr were performed for each ion-detection procedure and beam intensity used for sample analysis. The means of the calibration suites were used as the normal reference compositions for  $\epsilon$ -value calculation. All tabulated errors are at the 2 $\sigma$  confidence level.

The errors reported for Faraday runs are "external" errors based on reproducibility of the corresponding calibration analyses, which are significantly larger than "internal" errors based on individual ratio measurements within one run. The Faraday errors are smaller than the Daly errors but are

TABLE 2. Chromium isotopic results for Orgueil.

Step/Treatment*	Percent <sup>†</sup> Total Cr	$\epsilon_{53}^{\ddagger}$	$\epsilon_{54}^{\ddagger}$
<b>O-I (bulk Orgueil 202 mg)</b>			
1	2.5% HAc RT 35 min	0.97	
2	50% HAc RT 1 d	12.7	2 ± 1
3	4N HNO <sub>3</sub> RT 5 d	69.2	1 ± 1
4	6N HCl RT 5 d	3.0	0 ± 1
5	6N HCl 36 °C 1 d	0.58	
6	6N HCl 80 °C 1 d	1.82	0 ± 1
7	Conc. HF/HCl 100 °C 1 d	2.47	-1 ± 1
8	Repeat step 7	0.04	0 ± 1
9	4N NaOH 80 °C 3 h	4.25	
10	HClO <sub>4</sub> 185 °C 2.5 h	5.0	0 ± 1
<b>O-III (bulk Orgueil 116 mg)</b>			
1	2.5% HAc RT 35 min	0.50	3 ± 1
2	50% HAc RT 1 d	23.9	1 ± 1
3	4N HNO <sub>3</sub> RT 5 d	58.3	0 ± 1
4	6N HCl RT 5 d	0.64	-1 ± 10
5	6N HCl 36 °C 1 d	0.36	-4 ± 25
6	6N HCl 80 °C 1 d	1.05	-2 ± 5
7	Conc. HF/HCl 100 °C 1 d	5.54	-1 ± 5
<b>O-II (Magnetic)<sup>§</sup></b>			
M1	6N HCl RT 2 d		0 ± 5
M2	6N HCl 40 °C 1 d		-7 ± 12
M3	6N HCl 80 °C 1 d		-8 ± 7
M4	9N HCl 80 °C 1 d		6 ± 8
<b>O-II (Nonmagnetic)<sup>§</sup></b>			
5	6N HCl RT 1 d		-3 ± 44
6 <sup>¶</sup>	6N HCl 40 °C 1 d		-6 ± 3
B <sup>§</sup>			-4 ± 5
A1 <sup>¶</sup>	6N HCl 80 °C 1 d		-2 ± 3

\*Reagent (HAc = CH<sub>3</sub>COOH), (RT = room temperature) and duration.

<sup>†</sup>Percentage of total Cr (from Table 1) dissolved in this fraction.

<sup>‡</sup>Thermal ionization analysis corrected for discrimination assuming normal <sup>50</sup>Cr/<sup>52</sup>Cr (Shields *et al.*, 1966). Ratios of <sup>53</sup>Cr/<sup>52</sup>Cr and <sup>54</sup>Cr/<sup>52</sup>Cr stated as  $\epsilon$ -value (parts in 10<sup>4</sup>) deviations from mean of terrestrial reagent calibrations with same ion detection procedure and beam intensity as sample. Errors are 2 $\sigma$ .

<sup>§</sup>Bulk sample O-II (97 mg) was leached in acetic and nitric acids, as were samples O-I and O-III; the residue was then separated into "magnetic" and "nonmagnetic" fractions by adherence to a magnetic stirring bar in NaOH slurry.

<sup>¶</sup>Also see Table 3.

<sup>¶</sup>After step 6, O-II (nonmagnetic) residue was split into A and B aliquots. The B analysis tabulated is for a small fraction of the B aliquot directly loaded (as a solid) on the mass spectrometer filament.

nevertheless large compared to what could be expected from the operating beam and also large compared to errors reported by other laboratories. This situation was found to be the result of a flaw in one of the voltmeters (subsequently replaced). The errors are reported conservatively and do not compromise any of our conclusions, since the effects of primary interest are relatively large and not quantitatively interpretable at the error limits. Errors reported for the Daly runs are "internal precision" errors representing reproducibility of ratios obtained within that run; "external errors" reflecting run-to-run reproducibility of the calibrations generally agree well with the internal errors and are also reasonably close (within ~25%) to the error limits determined by Poisson statistics for the number of ions detected.

Sample size permitting, several samples were run in replicate analyses. In these cases, the compositions listed in Table 2 are means of all the analyses for that sample. The listed error limits are single-run external precision values. This is a conservative statement, made in preference to the lower values that follow from statistical convergence of the mean, because we cannot assess at what level below single-run precision systematic errors will dominate. Nevertheless, some of the errors given in Table 2 are overestimates, and deviations from normal composition are actually more robust than

they may seem. Two cases are particularly relevant: the  $^{53}\text{Cr}$  excesses in the acetic acid fractions of O-I and O-III are well resolved, as is the  $^{53}\text{Cr}$  deficiency in O-II-6 (see Table 3, Fig. 5, and accompanying discussion below).

### Interferences and Artifacts?

Because of the unusual nature of the observed isotopic effects (*i.e.*, pervasive effects at one isotope and no known correlative effects in other elements), particular attention must be given to the possibility of an artifact, such as an undiagnosed interference, consistently appearing in our own results as well as those of Rotaru *et al.* (1992). We note that because of the need for discrimination corrections in thermal ionization analysis, an artifact could arise from interference at either of the normalizing isotopes ( $^{50}\text{Cr}$  and  $^{52}\text{Cr}$ ) as well as at  $^{54}\text{Cr}$  itself. Specifically, an interference at mass 50 would lead to a false positive anomaly at 54 (and a false positive anomaly, half as big, at 53), and an interference at mass 52 would lead to a false negative anomaly at 54 (and a false negative anomaly, three-fourths as big, at 53).

The obvious isobaric interferences are  $^{54}\text{Fe}$  and  $^{50}\text{Ti}$ . Corrections for  $^{54}\text{Fe}$  were made by measuring mass 56 as part of the normal data collection procedure and assuming the 56 to be  $^{56}\text{Fe}$  with normal  $^{54}\text{Fe}/^{56}\text{Fe}$ . An Fe beam was often present, but the corrections to  $^{54}\text{Cr}$  were quite modest (a few  $\epsilon$ -units or less) in the Daly analyses and negligible (a few parts per million) in the Faraday analyses. The normal data collection algorithm does not include any  $\text{Ti}^+$  measurement, and no corrections were made at mass 50. Nevertheless, we scanned the  $\text{Ti}^+$  region frequently but never observed any beam identifiable as  $\text{Ti}^+$ , nor would any  $\text{Ti}^+$  beam be expected under operating conditions for Cr.

We can also eliminate hydrocarbons as a source of undiagnosed interference. In normal operating conditions, mass resolution is sufficient to render hydrocarbons almost fully resolved and quite visibly separate from Cr peaks. We never observed any hydrocarbons at Cr masses, even when specifically sought at higher resolution (with narrowed collector slit).

Particularly considering the presence of B in the sample load, it is also necessary to consider other potential molecular interferences. The specific cases of  $\text{LiBO}_2^+$  and  $\text{MgBO}_2^+$  can be eliminated since they would produce peaks at masses 49 or 51, which are not present in our analyses. It is possible to imagine other molecules with masses of 50, 52 or 54, but we find no evidence to support their presence.

It is also possible to argue from plausibility. Generation of false excesses at  $^{54}\text{Cr}$  by interference at mass 50 can be excluded because there are no corresponding apparent excesses of the right magnitude at  $^{53}\text{Cr}$ . Generation of false deficits of  $^{54}\text{Cr}$  by interference at mass 52 seems implausible because it would require coincidentally an interference at mass 53 of the right magnitude to mask the correlating deficit. We also consider it implausible that artifacts would conspire to produce false  $^{54}\text{Cr}$  deficits in some samples and excesses in others in the right proportions to generate an approximately normal mass balance. We never observed significant drift in calculated isotopic ratios, which is a common characteristic of an undiagnosed interference. As a final note, we intentionally have no Cr spikes in this laboratory, so there is no possibility of generating artifacts by spike contamination.

### Scanning Electron Microscope Characterizations

As noted above, both dissolution residues and dried solutions were inspected by SEM. More quantitative characterization of Cr-rich constituents was conducted on a polished thick section of Orgueil (no chemical processing) prepared by Nat Saenz of Battelle NW. This sample was studied with an automated x-ray mapping technique previously described by Swan *et al.* (1989). Magnification, electron beam step size and other parameters were selected such that all Cr-rich grains of  $>1\ \mu\text{m}$  would be detected with essentially unit efficiency (smaller grains would also be detected but with efficiency decreasing with size). Fifty-six adjacent  $215\ \mu\text{m} \times 215\ \mu\text{m}$  Cr x-ray maps and accompanying backscatter images were produced at  $400\times$  magnification. Nine randomly selected maps were found to yield an average of eight Cr-rich candidate grains each.

This suite of maps enabled evaluation of spatial distributions and comparison of elemental abundances. Each Cr-rich candidate grain was individually mapped and imaged at  $15,000\times$  in its detected elements (typically some subset of O, Si, Mg, P, S, Fe along with Cr).

## RESULTS

### Sample Chemistry

Chemical compositions of the various leach fractions are presented in Table 1. They are stated as elemental concentrations in the whole rock (*i.e.*, the starting bulk sample). The distribution of selected elements among these fractions for O-I and O-III is illustrated by stacked bar graphs in Fig. 1. The patterns for O-I and O-III are

quite similar. The major features of this distribution are that even dilute acetic acid dissolved substantial fractions of Mg, Ca, Ni and Sr and that the first three steps together (acetic and moderately weak nitric acids) dissolved essentially all the Mg, Ca, Ni and Sr and most of the Fe, Al and Cr. As noted above, the residue after step three of O-III was apparently  $\sim 36\%$  of the starting weight. A major phase present at this stage (*i.e.*, after the acetic and nitric acid steps) is magnetite, which accounts for  $\sim 10\%$  of the bulk meteorite (cf., Jeffery and Anders, 1970; Hyman and Rowe, 1983). The rest must have been composed primarily of the major elements for which we have no concentration data (*i.e.*, O, Si and S). Even these elements, however, should have been contained largely in alteration phases dissolved in the early leaching steps (an inference also supported by SEM analysis of the dried solutions).

### Anomalies in Chromium-54

Chromium isotopic results are presented in Tables 2 and 3 and illustrated in Figs. 2–5. Overall, the pattern of isotopic data is qualitatively very similar to those obtained for Orgueil and other CI meteorites by Rotaru *et al.* (1992). In the two bulk samples O-I and O-III, every dissolution fraction has anomalous  $^{54}\text{Cr}$ : a deficiency of  $\sim 6\ \epsilon$  in the most easily dissolved (acetic and nitric acids) fractions, which also account for most ( $>80\%$ ) of the Cr in the whole rock, and stronger excesses in the subsequent fractions representing more

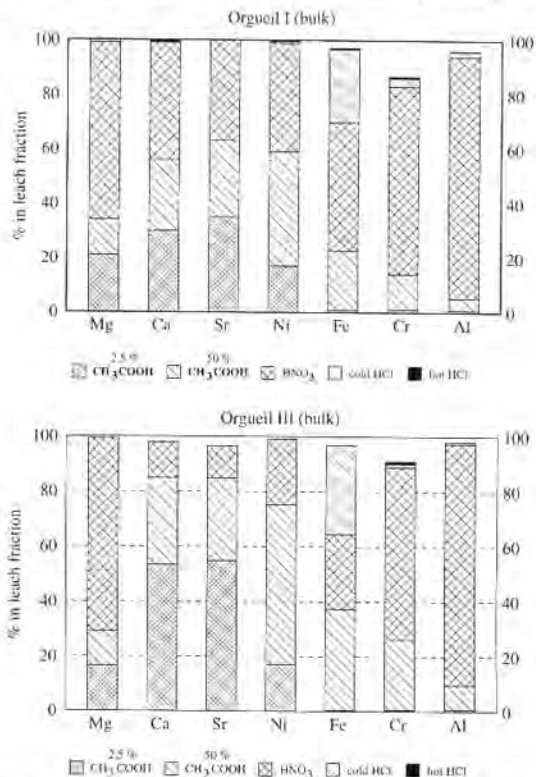


Fig. 1. Stacked bar graphs illustrating distribution of selected cations dissolved in sequential chemical attack of whole-rock Orgueil samples O-I (top) and O-III (bottom). Data are from Table 1 (ID data for Ca and Sr in O-I, otherwise ICP data); percentages are computed relative to the summed concentrations for each sample.

chemically resistant hosts (Fig. 2). It should be noted explicitly, however, that the largest excesses of  $^{54}\text{Cr}$  do not occur in the most chemically resistant phases. The residue from dissolution of major silicate phases in HF/HCl, containing very resistant phases such as spinels, still contains a significant fraction (Tables 1 and 2) of the whole rock inventory of Cr. The corresponding dissolution steps still contain well-resolved  $^{54}\text{Cr}$  excesses, but the excesses are smaller than in preceding fractions. It is unclear, however, whether this excess might be attributed to minor amounts of the most strongly anomalous phases that were not completely dissolved in the HCl and HF/HCl treatment, that is, we cannot rule out the possibility that the most refractory Cr-bearing phases (spinel?) are isotopically normal (or even have  $6\epsilon$  deficiencies like the most easily dissolved phases).

It is noteworthy that the positive anomalies first appear and are strongest in HCl dissolution steps. (Rotaru *et al.*, 1992, used equivalent acetic, nitric and HF/HCl steps but not the intermediate HCl steps, so in their data the positive anomalies first appear in the HF/HCl steps.)

Results for O-II magnetic and nonmagnetic fractions are illustrated in Fig. 4. Excesses of  $^{54}\text{Cr}$  appear in the expected fractions (*i.e.*, in treatment with HCl). In both cases, the effects are larger than in either bulk sample (O-I and O-III); possibly this reflects only simple sample inhomogeneity, but it also may reflect dissolution of additional near-normal Cr in NaOH during the magnetic separation. The appearance of comparable isotopic effects in both fractions seems to indicate that the magnetic separation process was ineffective in separating the high- $^{54}\text{Cr}$  carrier. In any case, it appears that the mag-

netite in the magnetic fraction is probably just a dilutant. Interestingly, the composition of the total Cr in sample O-II-B, as presumably reflected by its direct-load analysis (Fig. 4), is nearly normal but still contains a component with strong  $^{54}\text{Cr}$  excess, as indicated by

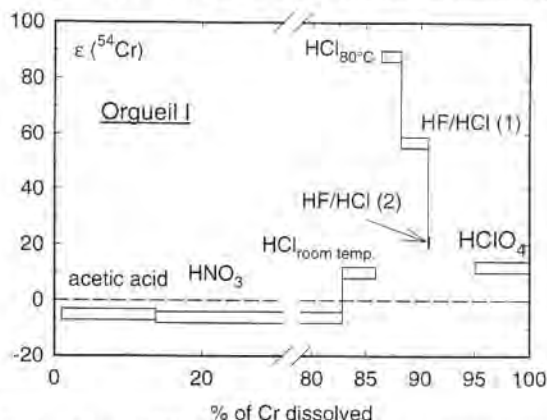


FIG. 3. Display of  $^{54}\text{Cr}$  anomalies (same as in Fig. 2) plotted against cumulative dissolved fraction of Cr for sample O-I. Data from Table 2. This display allows a better appreciation of how much Cr bears a given anomaly. Note break in abscissa scale.

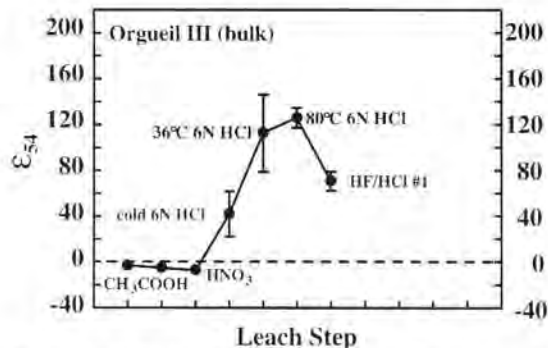
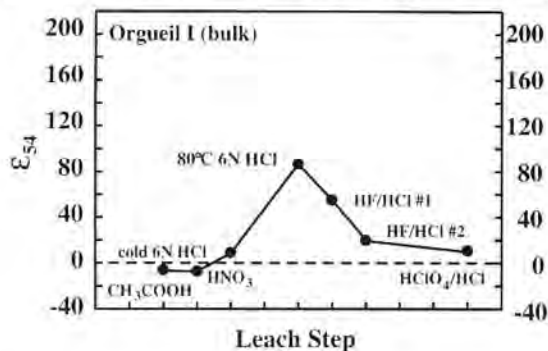


FIG. 2. Display of  $^{54}\text{Cr}$  anomalies plotted against sample number (sequence of progressive leach/dissolution steps) for whole rock Orgueil samples O-I (top) and O-III (bottom). Data from Table 2.

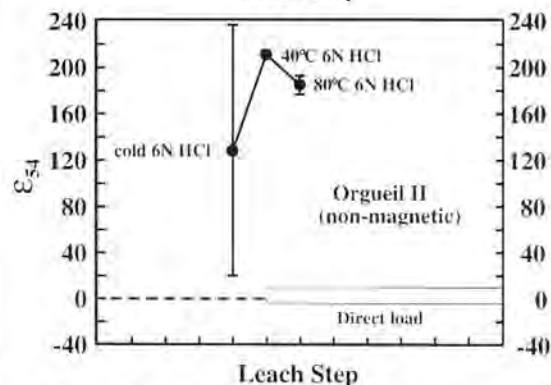
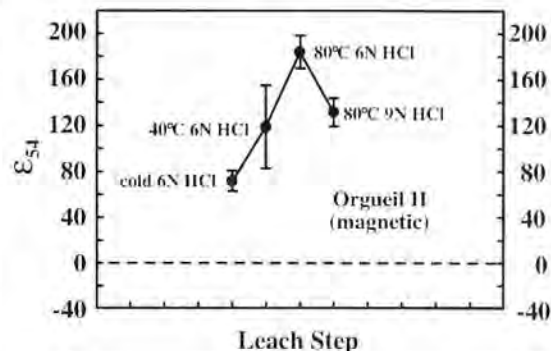


FIG. 4. Display of  $^{54}\text{Cr}$  anomalies plotted against dissolution sequence (*cf.*, Fig. 2) for "magnetic" (top) and "nonmagnetic" (bottom) fractions of Orgueil sample O-II. The "direct load" field (bottom) shows the results of direct load analysis of a small portion of the residue from O-II-6 (6N HCl at 40°C).

the analysis of sample O-II-A1, obtained by HCl leaching of the comparable O-II-A residue. Comparison with the O-I data indicates that the quantity of Cr extracted in HCl is small compared to the less anomalous Cr, which survives through this level of processing and which we presume dominates the direct-load analysis, but the effect warrants further investigation.

#### Anomalies in Other Isotopes of Chromium?

The Cr data reported by Rotaru *et al.* (1992), along with most of the data reported herein, show resolved anomalies only for  $^{54}\text{Cr}$ , which suggests the view that the anomalous component is essentially monoisotopic  $^{54}\text{Cr}$ . Some of the present data indicate that this is not quite true, however. There are small (1–2  $\epsilon$ ) but real excesses of  $^{53}\text{Cr}$  in the acetic acid fractions of O-I and O-III; these are probably not anomalies, however, but rather excesses from the decay of  $^{53}\text{Mn}$  (cf., Rotaru *et al.*). The deficiency of  $^{53}\text{Cr}$  in O-II-6 cannot be thus explained away.

Table 3 lists individual spectrometer runs (all pulse-counting Daly on the Sector 54) for the "nonmagnetic" samples O-II-6 and O-II-A1, the two samples that have the highest  $^{54}\text{Cr}$  anomalies thus far observed. The subset of these data representing runs at 400 keps ( $4 \times 10^5$  counts/s on the Daly detector) of  $^{52}\text{Cr}$  (the rest were taken at 250 keps) is shown in Fig. 5, along with the calibration suite of terrestrial reagent analyses at 400 keps. Because of beam instabilities, most of the sample runs have stated errors (based on internal statistics) somewhat larger than those of the calibrations, which is also evident in run-to-run reproducibility. It would be difficult to assert a  $^{53}\text{Cr}$  anomaly from a single run, but if convergence of the mean in replicate analyses is valid, then these results indicate a  $^{53}\text{Cr}$  anomaly at least in O-II-6, a deficiency of  $\sim 6 \epsilon$ .

The data in Table 3 and Fig. 5 also suggest a  $^{53}\text{Cr}$  anomaly, a deficiency of  $\sim 2 \epsilon$ , in O-II-A1, but the evidence is much weaker than for O-II-6; without the O-II-6 data, the O-II-A1 data would likely not attract attention as being significantly different from normal. The more relevant point is that the anomaly in O-II-A1, if there is one at all, is not very large. If anomalies in  $^{53}\text{Cr}$  scaled with those in  $^{54}\text{Cr}$ , then taking O-II-6 as a base, we would expect that O-II-A1 should have a 5  $\epsilon$  deficiency of  $^{53}\text{Cr}$ , a prediction that is not supported by the data.

Two alternative interpretations of the  $^{53}\text{Cr}$  deficit in O-II-6 are possible. One, as described below, is in terms of isotopic anomaly,

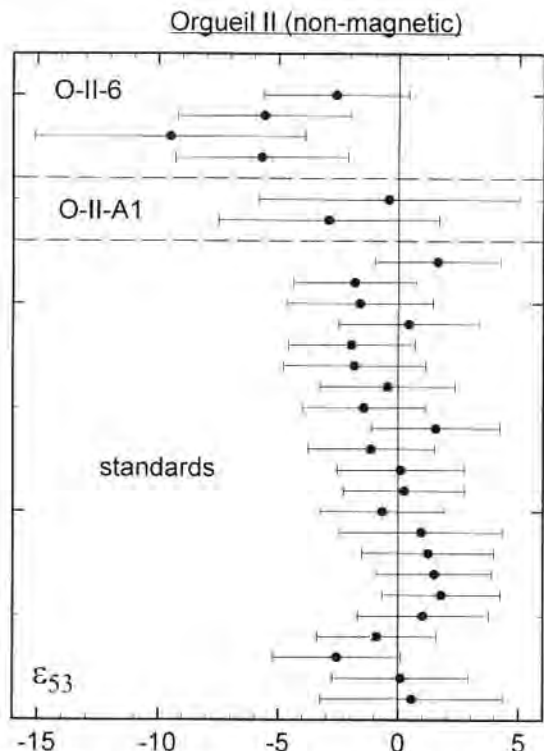


FIG. 5. Slinky diagram showing  $^{53}\text{Cr}$  data in Sector 54 single-collector pulse-counting Daly runs for O-II-6 and O-II-A1 at 400 keps of  $^{52}\text{Cr}$  (subset of data in Table 3), plus the calibration suite of 22 analyses of terrestrial Cr at the same beam intensity acquired before, between and after sample analyses (1995 April–August); horizontal bars show  $2\sigma$  "internal" errors. A "run" comprises 100 "sets," each with 5 "ratios" (one cycle over all isotopes integrating each for 5 s) at the nominal beam intensity (a full run requires 9–10 h). The standard deviation for the calibration suite ("external" precision) is 1.33  $\epsilon$ , which is slightly higher than the limit (1.26  $\epsilon$ ) imposed by Poisson statistics for the number of ions detected. The reference composition is the mean of the calibrations, for which  $^{53}\text{Cr}/^{52}\text{Cr}$  (with  $^{50}\text{Cr}/^{52}\text{Cr}$  normalization) is 1.52  $\epsilon$  lower than the value reported by Papanastassiou (1986).

TABLE 3. Replicate analyses\* of selected samples of Orgueil.

Sample	$\epsilon_{53}^{\dagger}$	$\epsilon_{54}^{\dagger}$
O II-A1	$-2 \pm 4$	$188 \pm 7$
	$-3 \pm 5$	$182 \pm 8$
	$0 \pm 3$	$186 \pm 5$
O II-6	$-4 \pm 3$	$213 \pm 7$
	$-9 \pm 3$	$204 \pm 7$
	$-7 \pm 3$	$209 \pm 6$
	$-6 \pm 4$	$205 \pm 8$
	$-6 \pm 4$	$218 \pm 7$
	$-9 \pm 6$	$211 \pm 10$
	$-6 \pm 4$	$215 \pm 8$
	$-3 \pm 3$	$217 \pm 5$

\*All analyses in pulse-counting Daly made on Sector 54 at either 250 keps or 400 keps.

<sup>†</sup>Errors stated at  $2\sigma$  level from "internal statistics."

in which case comparison of O-II-6 and O-II-A1 indicates the need for at least two anomalous component compositions. The alternative is that the  $^{53}\text{Cr}$  deficit is not an anomaly but a "ghost," reflecting formation with low Mn/Cr at an early time before decay of  $^{53}\text{Mn}$  made its contribution to present normal Cr. The highest  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio yet reported for solar system materials, however, is  $4.4 \times 10^{-5}$  (Birek and Allègre, 1988), which corresponds to 3  $\epsilon$  of present  $^{53}\text{Cr}$ .

Correction for instrumental discrimination in thermal ionization spectrometry requires the assumption that at least one isotope ratio is a known constant. We have here adopted the conventional (but arbitrary) selection of  $^{50}\text{Cr}/^{52}\text{Cr}$  for the normalization ratio. When more than one isotope has an apparently anomalous abundance, however, this (or any other) choice cannot be defended without additional evidence; indeed, there may be no "normal" ratio that can be predicted beforehand. Unless the anomalies are large compared to plausible instrumental discrimination effects, it is not even possible to assert definitively which isotopes (if not all of them) are present in an inferred anomalous component. The apparent excesses of  $^{54}\text{Cr}$

are large compared to apparent effects at other isotopes and to discrimination effects, so there is little doubt about the presence of an anomalous component enriched in  $^{54}\text{Cr}$ . If the anomalous component is viewed as being or involving nearly monoisotopic  $^{54}\text{Cr}$ , however, it cannot have a negative abundance of  $^{53}\text{Cr}$ , in which case the  $^{53}\text{Cr}$  deficiency must be seen as an artifact resulting from the data reduction procedure. A more plausible interpretation is that the anomalous component is also enriched (relative to normal) in  $^{52}\text{Cr}$ . If we were to assume that the anomalous component contained only  $^{54}\text{Cr}$  and  $^{52}\text{Cr}$  (equivalently, if we normalize by  $^{53}\text{Cr}/^{50}\text{Cr}$ ), then sample O-II-6 would have  $\sim 4 \epsilon$  excess  $^{52}\text{Cr}$  and an additional  $8 \epsilon$  excess  $^{54}\text{Cr}$  (i.e., a total anomaly of  $219 \epsilon$ ). If this deconvolution is correct, the  $^{54}\text{Cr}/^{52}\text{Cr}$  ratio in the anomalous component is approximately unity, a result which may be useful in constraining nucleosynthetic models for its production.

### Chromium-rich Grains

The absence of correlative anomalies in other elements suggests that the  $^{54}\text{Cr}$ -enriched carrier is also chemically enriched in the element Cr. Examination by SEM indicates that there are indeed Cr-rich grains in the nitric acid residues of Orgueil (Podosek *et al.*, 1995), which are typically submicrometer in size. In general, EDX analysis indicates that the principal elements in such grains are Cr and O, but there appear to be different kinds of Cr-O grains, since some show only Cr and O while others have variable but significant amounts of Fe, Mg and/or Mn. (But it is possible that these elements are not actually in the Cr-O grains if the excitation volume in EDX analysis is larger than the grains.) In principle, it could be argued that some such grains result from the initial chemical treatment, but this cannot be the general case since Cr- and O-rich grains have also been found in unprocessed Orgueil (Podosek *et al.*, 1995). Greshake and Bischoff (1996) have also examined Cr- and O-rich grains in unprocessed Orgueil; besides chromite ( $\text{FeCr}_2\text{O}_4$ ), they have identified three other Cr-rich phases: magnesiochromite ( $\text{MgCr}_2\text{O}_4$ ), chromium oxide ( $\text{Cr}_2\text{O}_3$ ) and ureyite ( $\text{NaCrSi}_2\text{O}_6$ ).

Although not hard to find, in absolute terms Cr-rich grains in the nitric acid residues are scarce, and it is difficult to determine their modal abundance with confidence; our best estimate is that they account for  $\sim 0.02\%$ . If this abundance is approximately correct, then such grains cannot be major carriers of whole rock Cr ( $\sim 0.26\%$ , see Table 1), but they could in principle provide the few percent of total Cr characterized by the greatest  $^{54}\text{Cr}$  excesses. Chromium-oxygen-rich grains are also found in the HCl residues, however, and we have not been able to determine with confidence whether their overall abundance, or the abundance of some subpopulation, is significantly reduced by the HCl treatment that liberates the most anomalous Cr.

We have made also x-ray maps of unprocessed Orgueil to identify Cr-rich grains. As in the residues, Cr- and O-rich grains are not difficult to find; a representative specimen is shown in Fig. 6. In maps covering some  $4 \times 10^{-3} \text{ cm}^2$ , the modal abundance of Cr- and O-rich grains of  $\sim 1 \mu\text{m}$  or greater in diameter is  $\sim 0.015\%$ , which is consistent with the observations in the nitric acid residues.

Mapping of unprocessed Orgueil also reveals the presence of other kinds of Cr-rich phases. We have observed a few each of sulfide and phosphide grains (Fig. 7). The abundance of these grains is about an order of magnitude lower than the Cr- and O-rich grains, but this estimate is based on only a few observations and is correspondingly uncertain. We have not observed Cr-rich sulfides or phosphides in the dissolution residues, but considering their scarcity, this is not significant.

Although Cr in Orgueil occurs mostly as a distributed trace/accessory element, there are clearly a variety of phases, accounting for a small part of the total Cr inventory, in which Cr is a major element. There has not yet been any unambiguous characterization of Cr isotopic composition in any of these phases. It also should be noted that known occurrences are only for approximately micrometer-sized grains; the possible population of significantly smaller grains remains essentially unexplored.

### DISCUSSION

The overall pattern of Cr anomalies exhibited by Orgueil, as well as other carbonaceous chondrites (Rotaru *et al.*, 1992), is that most of the Cr, specifically that dissolved in acetic and nitric acids, has a nearly uniform composition with a relatively small deficit in  $^{54}\text{Cr}$ ,  $\epsilon_{54} \approx -5$ . A small fraction of the total Cr, not dissolved until the hydrochloric acid steps, has a larger and more variable excess of  $^{54}\text{Cr}$ . It is logical to enquire whether these effects cancel. For O-I, the sample for which we have the most complete data, mass balance indicates that they do: the whole rock composition calculated by summing the dissolution fractions is  $\epsilon_{54} = -1$ , nil within errors. Thus, at least to first order, bulk Orgueil has normal  $^{54}\text{Cr}$  composition, even though no significant Cr host phase within Orgueil has normal composition. Since no known process operating within the solar system can produce the observed isotopic anomalies, these variations must reflect the variety of stellar nucleosynthetic processes that have contributed to solar system materials. The inference of normal Cr composition in bulk Orgueil thus translates to the inference that Orgueil contains approximately the "normal" mix of presolar nucleosynthetic components, but that they are simply not homogenized, and can be partially separated by selective chemical attack.

Rotaru *et al.* (1992) seemingly favor a model in which meteorites such as Orgueil are composed of a variety of mineralogically distinct (Cr-bearing) grains that preserve their presolar nucleosynthetic signatures in variable isotopic compositions. We consider such an extreme view unnecessary and implausible. It is well established that refractory inclusions, particularly constituent spinel, in the CV3 meteorite Allende characteristically contain heavy Cr, with  $\epsilon_{54}$  in the range  $+5$  to  $+10$  (Birck and Allègre, 1984, 1988; Papanastassiou, 1986; Papanastassiou and Brigham, 1989). The existence of such materials in Orgueil has not been established but would not be surprising, and it may be that chemically refractory phases such as spinel are involved in the relatively modest  $^{54}\text{Cr}$  enrichments seen in the final steps of O-I (Figs. 2 and 3). Spinel/chromite cannot account for the largest  $^{54}\text{Cr}$  enrichments, however, since they would not likely suffer significant dissolution in hydrochloric acid. Some other phase, hereafter denoted the "mystery" phase, must be responsible for the major isotopic effects evident in Figs. 2-4. Excess  $^{54}\text{Cr}$  is characteristic of only a small fraction of the total Cr inventory (Figs. 1 and 3), however, and there is no evidence for significant isotopic variation in the majority of the Cr. Considering that phyllosilicates evidently account for most of the Cr in the whole rock (Kerridge, 1976), it would be surprising to find any preserved isotopic variation in this major component. We think the more plausible view is that most of the Cr in Orgueil is a homogenized mixture of presolar nucleosynthetic components, a mixture that would be isotopically normal but for lack of the heavy Cr in the mystery phase. The isotopic mixing could have occurred in nebular processing prior to accretion of the Orgueil parent body, but even if it did not, it could have occurred during aqueous alteration in the parent body. (The potential relevance to the overall mass balance of very resistant phases such as spinel remains to be determined.)

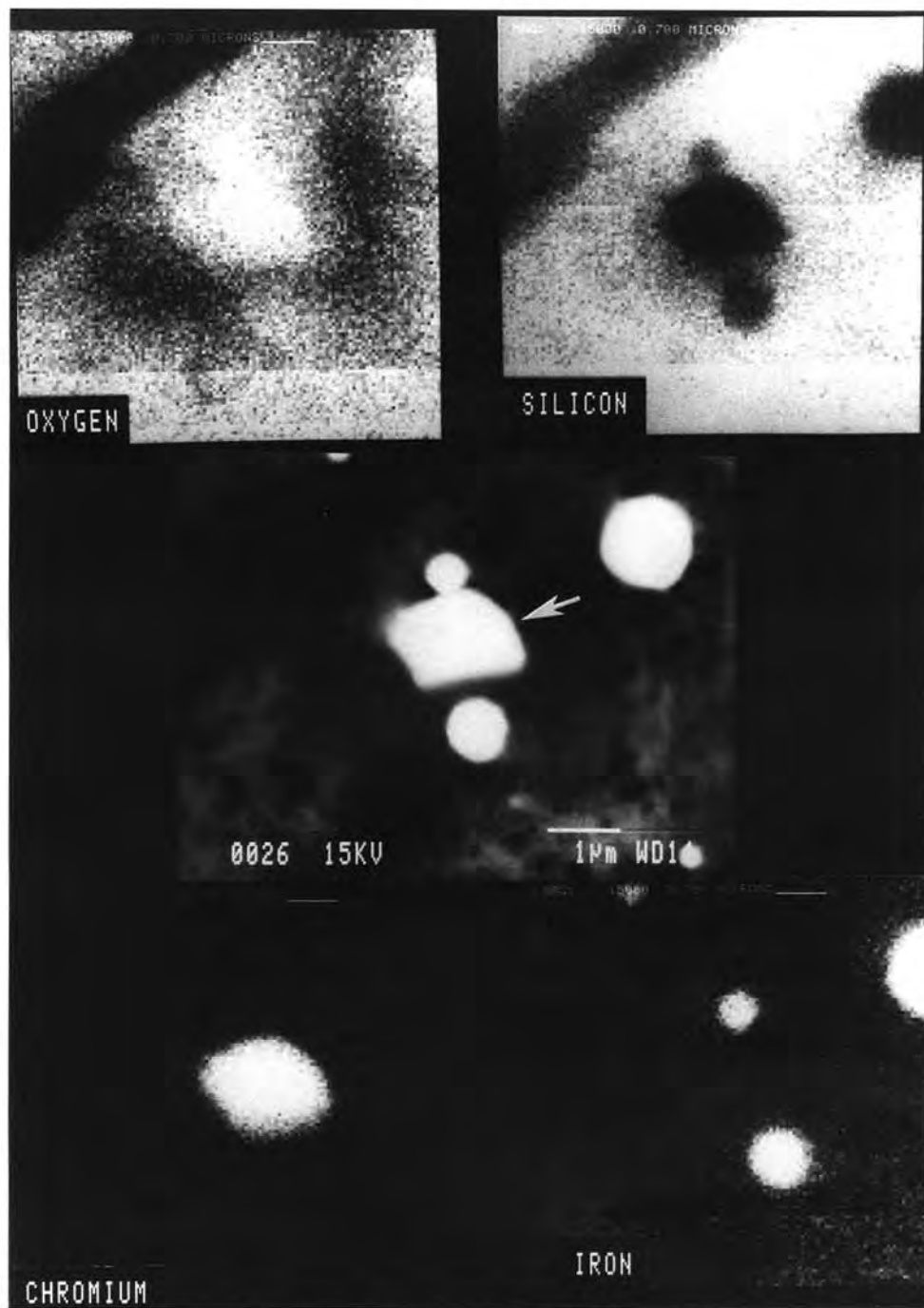


FIG. 6. A Cr- and O-rich grain in an unprocessed thick section of Orgueil. The central frame is a backscatter image; peripheral frames are x-ray maps of the same area for the indicated elements.





FIG. 7. Chromium-sulfur-rich and Cr-P-rich grains in Orgueil. Compare to Fig. 6.

The nature of the inferred mystery phase can be constrained only circumstantially: it must have remained aloof, resisting isotopic exchange with phases bearing most of the Cr, during both nebular and parent body processing, but it must also be substantially soluble in hydrochloric acid. It also likely undergoes isotopic equilibration with its surroundings at only modest temperatures (300–400 °C). This follows from the observation of Cr anomaly patterns in CM meteorites that are qualitatively similar to but more subdued than those in CI meteorites such as Orgueil and only vestigial to nil effects in CO and CV meteorites (Rotaru et al., 1992). On the premise that these other meteorite classes also contained initially unhomogenized heavy Cr similar to that in the CI meteorites, the inference is that the anomalies were eroded in the relatively mild thermal metamorphism experienced by these classes (also see Rotaru et al., 1992). It can also be inferred that the mystery phase is relatively enriched in the element Cr. This follows from the likelihood that other elements besides Cr are isotopically anomalous in this phase and that the absence of known correlative anomalies in other elements reflects lesser dilution by normal host materials for Cr than for other elements. (Actually, anomalies have been sought and not found only for nucleosynthetic Fe-group elements (Rotaru et al., 1992); correlating anomalies may exist in other elements not yet examined.) If our conclusion of variable anomalous Cr composition (Fig. 5) is correct, there may be more than one mystery phase, but it is also possible that there is only one type of phase but different samples of this phase have different isotopic compositions.

One obvious possibility is that the mystery phase is a preserved type of interstellar grain that is analogous to several varieties known in other meteorites (cf., Anders and Zinner, 1993). If so, it would differ importantly from the other types in not being very resistant to chemical attack (preparation of samples of the presently known types involves their resistance to reagents that destroy nearly all other meteoritic constituents) as well as in thermal stability and so would impose much more severe constraints on entry into and processing within the solar nebula (cf., Chick and Cassen, 1996) than do the known varieties. Also, if it is an interstellar phase, its Cr is likely to be radically anomalous (i.e., isotopically very different from normal) and the modest effects yet observed would indicate major dilution with more nearly normal Cr. There need be but very little of a radically anomalous carrier. To account for some  $5 \times 10^{-4}$  of the  $^{54}\text{Cr}$  in the whole rock, for example, grains containing, say, 25%  $^{54}\text{Cr}$  need have a modal abundance of only  $10^{-7}$ ; chemically nonresistant grains at this abundance would obviously be difficult to find.

It cannot be unambiguously concluded that the mystery phase is interstellar, however. Although large in many respects, the anomalies thus far observed are still small in absolute terms (i.e., only ~2%) and do not demand an interstellar interpretation. There are ample instances of objects that are generally believed to have formed in the solar nebula but to have incorporated presolar nucleosynthetic components in proportions marginally different from those that define solar normal and so to exhibit significant but still modest isotopic anomalies (e.g., Ireland, 1990). Indeed, as noted above, Cr is one of the elements displaying such anomalies (Birck and Allègre, 1984; Papanastassiou, 1986), and the postulated mystery phase could be another instance of the same phenomenon. Known objects of this kind are all "refractory," however, and believed to have formed in high-temperature nebular events. The mystery phase is evidently not a "high-temperature" product and so would probe a different regime of nebular history than the known objects of this kind. There could

also be more of it. If the heavy Cr carrier were, say, 25% Cr with  $^{54}\text{Cr}$  enrichment little greater than  $\epsilon_{54} \approx +210$ , the lower limit set by observation, the same logic as above leads to a modal abundance of ~0.02%.

The presence of Cr- and O-rich grains at about this level of modal abundance is certainly suggestive. Nevertheless, we doubt that this assemblage as a whole is the carrier of excess  $^{54}\text{Cr}$  at anomaly levels close to those observed in the dissolution fractions. The principal argument is dissolution characteristics. Even though acid solubility of chromium oxides can be evidently rather variable according to formation conditions and can sometimes include solubility in HCl (Gmelin, 1962), we would expect that most of these grains would survive the treatments that bring the largest anomalies into solution. This expectation is reinforced by the observation that there is no gross difference in the evident population of Cr- and O-rich grains in residues before and after the steps in which the anomalies appear most prominently. This objection does not apply, of course, to the hypothesis that the mystery carrier is an oxide or silicate constituting a small subpopulation of the Cr- and O-rich grains, nor that it is a subpopulation of the much less abundant sulfide and/or phosphide phases. It should be noted that a hypothesis of less abundant phases requires correspondingly greater anomalies, thus swinging the evidence toward the interstellar grain interpretation. Unfortunately, there are as yet no direct isotopic data unambiguously associated with any of these phases that would support or refute their candidacies as heavy Cr carriers. This discussion must also be qualified by the possibility of other Cr-rich phases sufficiently scarce or sufficiently small as to have thus far evaded detection. A speculative but obvious possibility is metal: Grossman and Olsen (1974), for example, describe relatively Cr-rich metal in CM chondrites, and while metal has not been reported in CI chondrites, it might be present at very low modal abundance or in very fine grains.

Finally, it would be well to maintain focus on the question, Why Cr? The short answer, as above, is mineralogical control, but this does not address the more basic question of why it should be a prominently Cr-bearing phase with the right chemical properties that survived nebular processing (or was made in the nebula). Appearance of this isotopic effect in Cr may just reflect a superposition of coincidences, but it may also be that the effect appears in other elements not yet surveyed or would appear with different chemical separation procedures.

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